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Supporting Information

for

One-pot Solvothermal Synthesis of Biocompatible Magnetic Nanoparticles Mediated by Cucurbit[n]urils

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1. Preparation and Syntheses

1.1 Materials and methods

$FeCl_3$ was purchased from Aladdin, and cucurbit[5]uril (CB[5]), cucurbit[6]uril (CB[6]), cucurbit[7]uril (CB[7]), cucurbit[8]uril (CB[8]), were synthesized and characterized according to literature procedures.[S1] The other chemicals were of analytical grade and used without further purification.

Scanning electron microscopy (SEM) images were recorded on a Hitachi SU8020 electron microscope operating at 20 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were taken with a JEM-2100F microscope (Japan) operated at 200 kV and the samples were first dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. Fourier transform infrared (FT-IR) spectra were collected on Bruker Fourier spectrophotometer using KBr pellets (USA). X-ray photoelectron spectroscopy (XPS) was operated at 0.46 eV on an ESCALAB 250 instrument (Thermo Fisher Scientific, USA). Thermogravimetric analysis (TGA) was taken with TA Q500 operated at 10 K min^{-1} at nitrogen atmosphere. Magnetic characterizations were carried out on a superconducting quantum interference device (SQUID) magnetometry. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab X-ray diffractometer. Deionized water produced by Experimental Water System (Lab-UV-20). Dynamic light scattering (DLS) experiments were performed on a Zetasizer Nano ZS instrument.

1.2 One-step solvothermal synthesis of CB[6]-MNPs at different temperatures

$FeCl_3$ (0.65 g, 4.0 mmol) and CB[6] (0.20 g, 0.2 mmol) were first dissolved in ethylene glycol (20 mL), and sodium acetate (NaAc, 1.20 g, 14.6 mmol) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclaves were heated at 190, 200, 210, 220, and 230 °C, respectively, and maintained for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for several times.

1.3 One-step solvothermal synthesis of CB[6]-MNPs at different time

$FeCl_3$ (0.65 g, 4.0 mmol) and CB[6] (0.20 g, 0.2 mmol) were first dissolved in ethylene glycol (20 mL), and NaAc (1.20 g, 14.6 mmol) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclaves were heated at 200 °C for 6, 8, 10, and 12 h, respectively, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for several times.

1.4 One-step solvothermal synthesis of CB[6]-MNPs at different ratios of $FeCl_3$ and CB[6]

$FeCl_3$ (0.4, 1.0, 2.0, and 4.0 mmol, respectively) and CB[6] (0.20 g, 0.2mmol) were first dissolved in ethylene glycol (20 mL), and NaAc (1.20 g, 14.6 mmol) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclaves were heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for several times.

1.5 One-step solvothermal synthesis of CB[n]-MNPs at different ring sizes of CB[n]s

$FeCl_3$ (0.65 g, 4.0 mmol) and CB[n] (n = 5-8, 0.2 mmol) were first dissolved in ethylene glycol (20 mL), and NaAc (1.20 g, 14.6 mmol) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclaves were heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for several times.

2. Materials Characterization

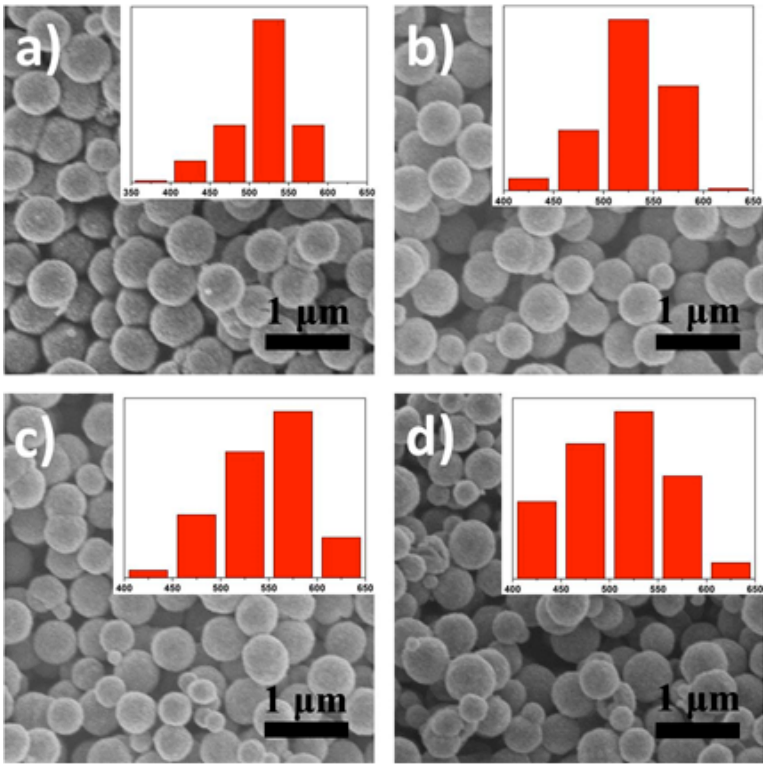

Figure S1. The SEM images and size distributions of CB[6]-MNPs synthesized by the typical solvothermal reaction with $FeCl_3$ (4.0 mmol), CB[6] (0.2 mmol), and NaAc (14.6mmol) in ethylene glycol (20 mL) for 10 h, and maintained at a) 200 °C, b) 210 °C, c) 220°C, and d) 230 °C.

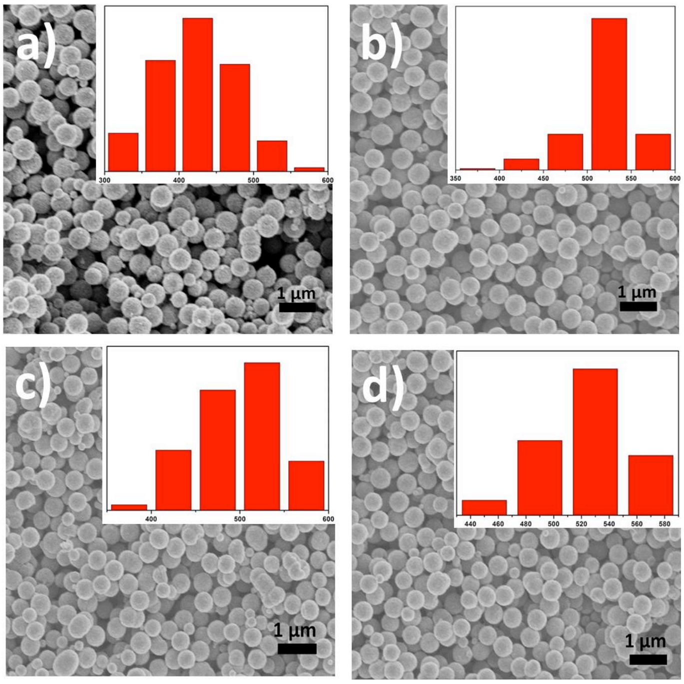

Figure S2. The SEM images and size distributions of CB[6]-MNPs synthesized by the typical solvothermal reaction with $FeCl_3$ (4.0 mmol), CB[6] (0.2 mmol), and NaAc (14.6mmol) in ethylene glycol (20 mL) at 200 °C for different reaction time: a) 6 h, b) 8 h, c) 10 h, and d) 12 h.

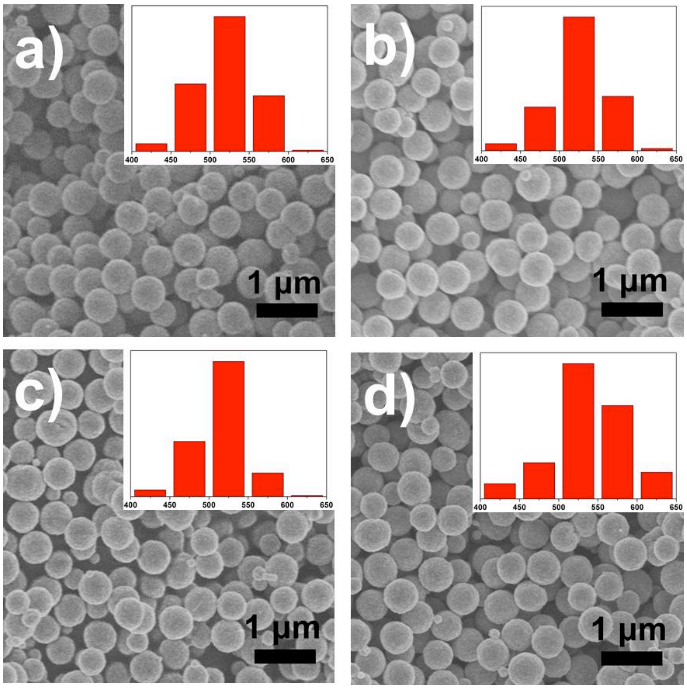

Figure S3. The SEM images and size distributions of CB[n]-MNPs: a) CB[5]-MNPs, b) CB[6]-MNPs, c) CB[7]-MNPs, and d) CB[8]-MNPs, synthesized by the typical solvothermal reaction with $FeCl_3$ (4.0 mmol), CB[n] (n = 5-8, 0.2 mmol), and NaAc (14.6 mmol) in ethylene glycol (20 mL) at 200 °C for 10 h.

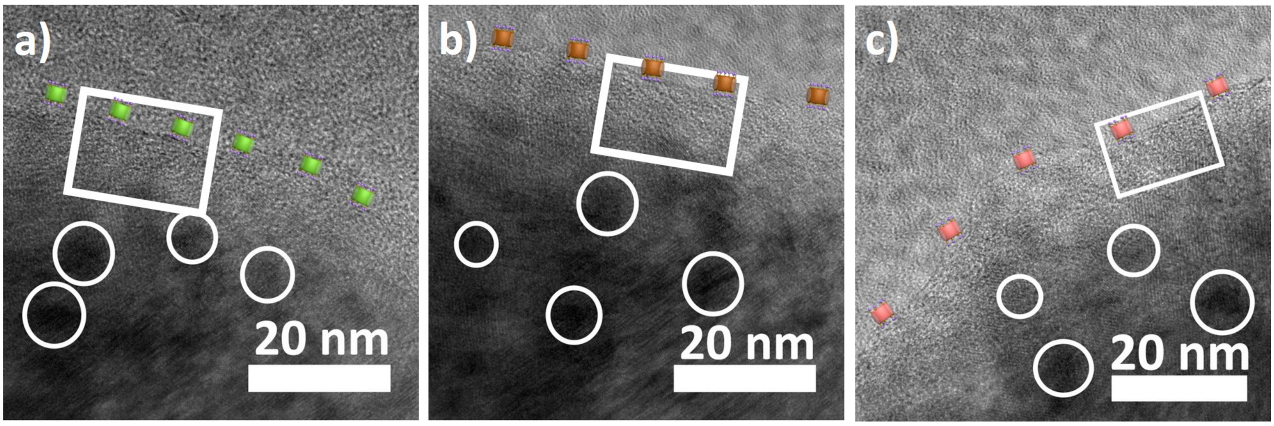

Figure S4. HRTEM images of the CB[n]-MNPs: a) CB[5]-MNPs; b) CB[6]-MNPs; c) CB[7]-MNPs, synthesized by the solvothermal reaction with $FeCl_3$ (4.0 mmol), CB[n] (0.2 mmol), and NaAc (14.6 mmol) in ethylene glycol (20 mL) at 200 °C for 10 h. The areas marked with cycles correspond to the crystalline and amorphous phase in the particles, suggesting that the primary magnetic nanoparticles in the large particle are connected with isolated clusters that are approximately composed of small primary crystals with a size of 6-8 nm and the area marked with a box is a layer of iron-containing complexes.

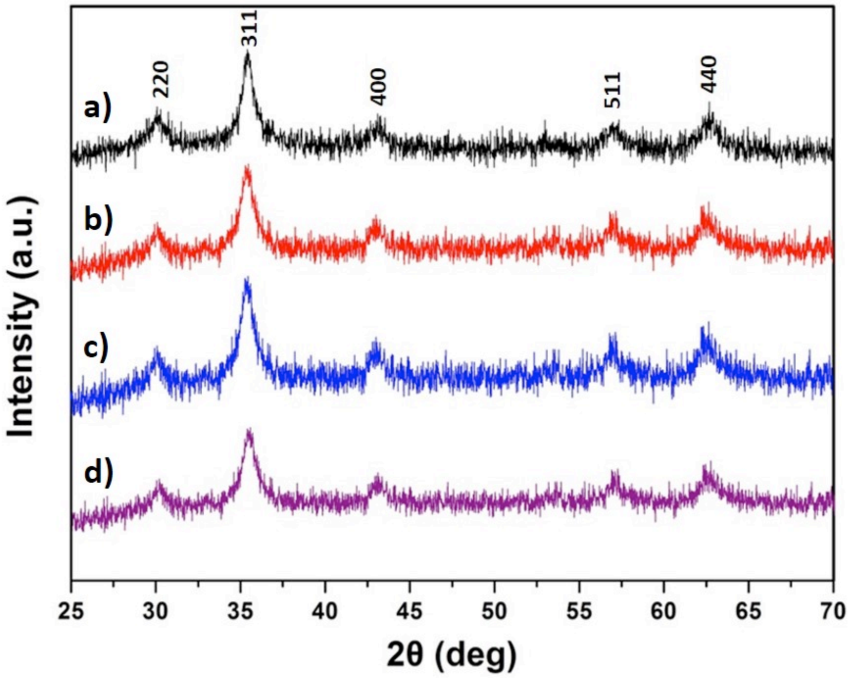

Figure S5. XRD patterns of CB[6]-MNPs obtained with different reaction time of a) 12 h, b) 10 h, c) 8 h, and d) 6 h.

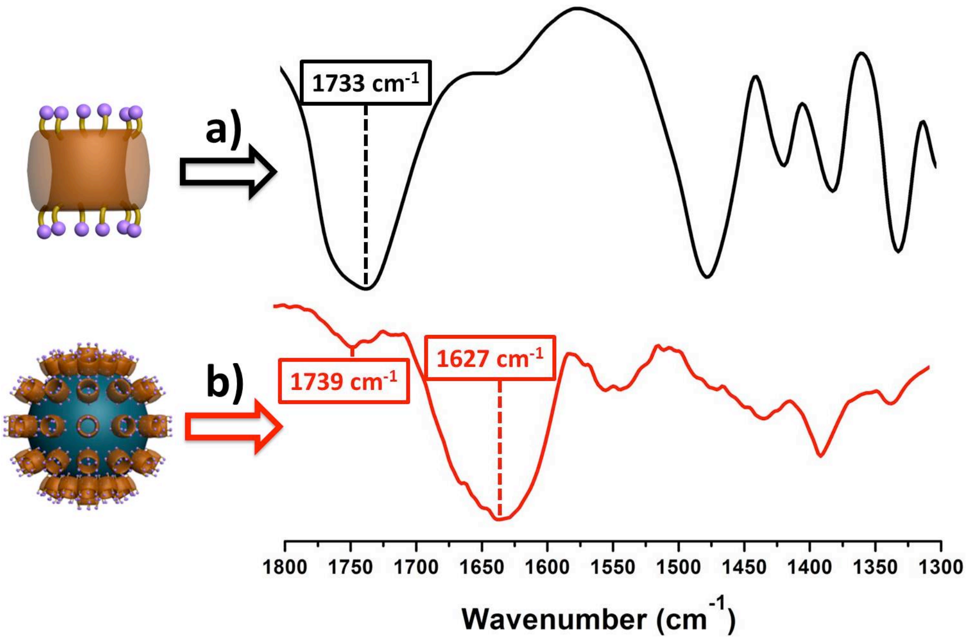

Figure S6. Selected area of FT-IR spectra of bared CB[6] (a) and CB[6]-MNPs (b), showing the changes of carbonyl absorption bands.

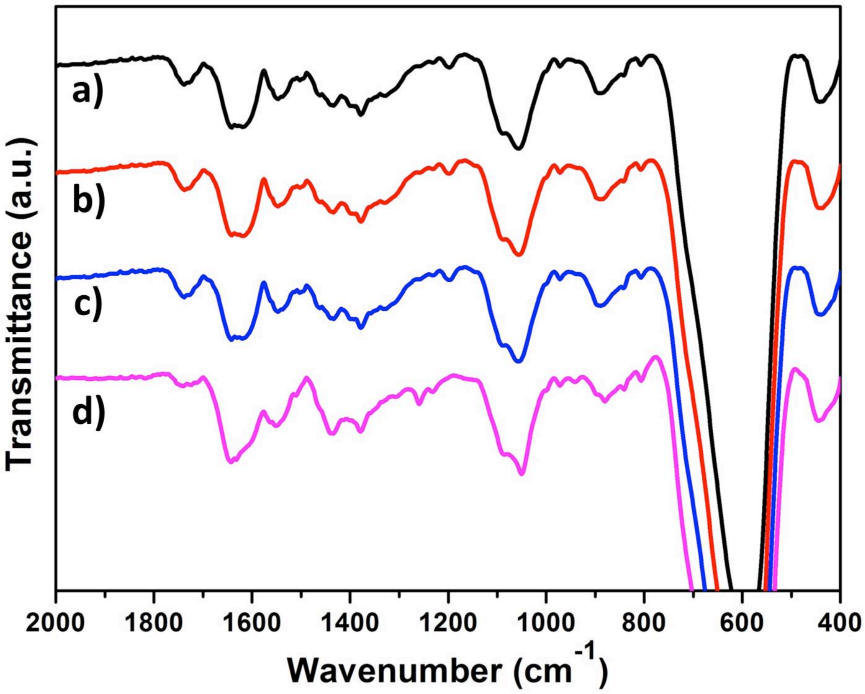

Figure S7. FT-IR spectra of a) CB[5]-MNPs, b) CB[6]-MNPs, c) CB[7]-MNPs and d) CB[8]-MNPs.

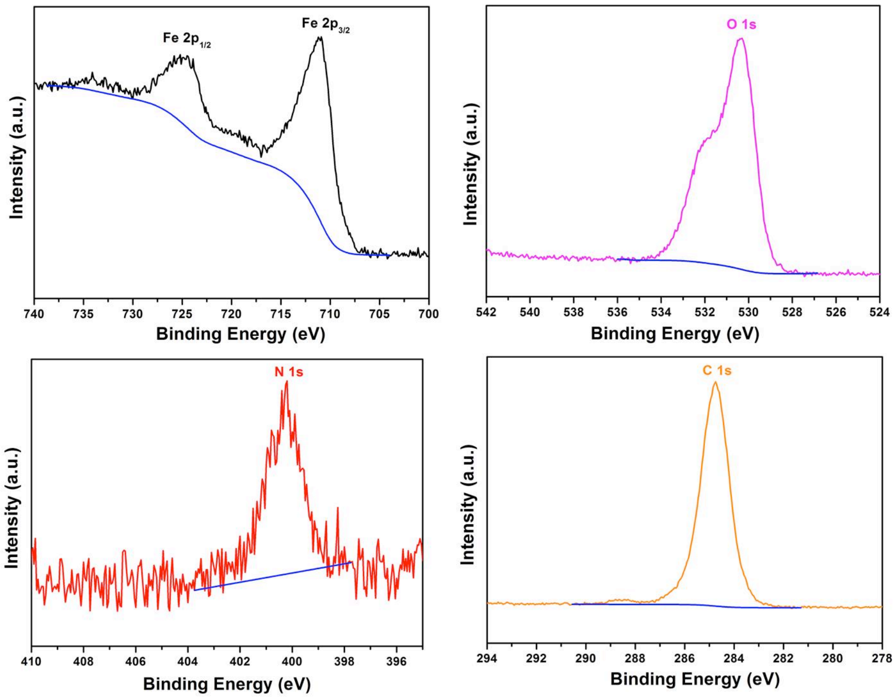

Figure S8. The XPS spectra of the CB[6]-MNPs synthesized with typical solvothermal reaction using $FeCl_3$ (4.0 mmol), CB[6] (0.2 mmol) and NaAc (14.6 mmol) in ethylene glycol (20 mL) at 200 °C for 10 h, which exhibited two peaks at 711.1 and 725.0 eV in good agreement with the known values of the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ in Fe_3O_4 respectively. Moreover, peaks at 530.3, 400.2, and 284.7 eV correspond to the peaks of O 1s, N 1s, and C 1s.

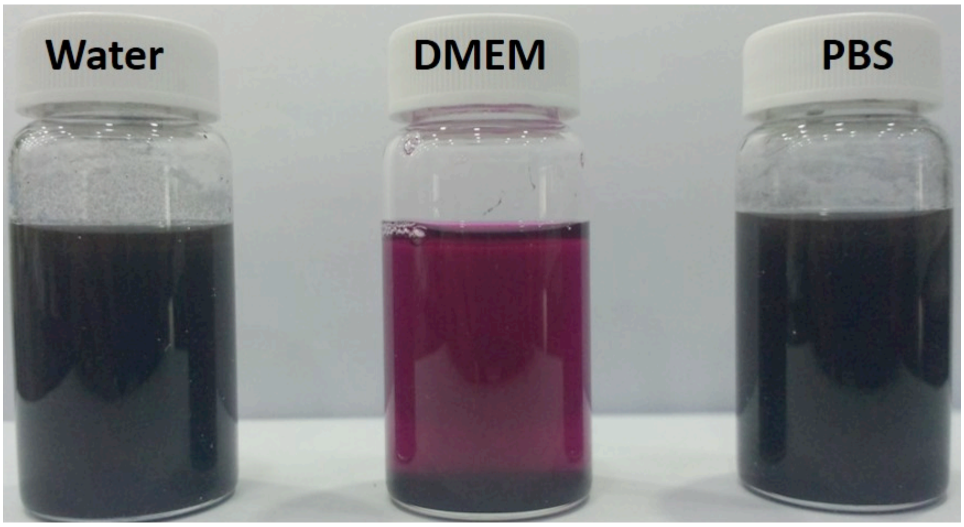

Figure S9. The CB[6]-MNPs can be easily dispersed in water, cell culture medium (DMEM) and phosphate buffer solution (PBS) to form a stable dispersion that can stand for more than two days without visible sedimentation.

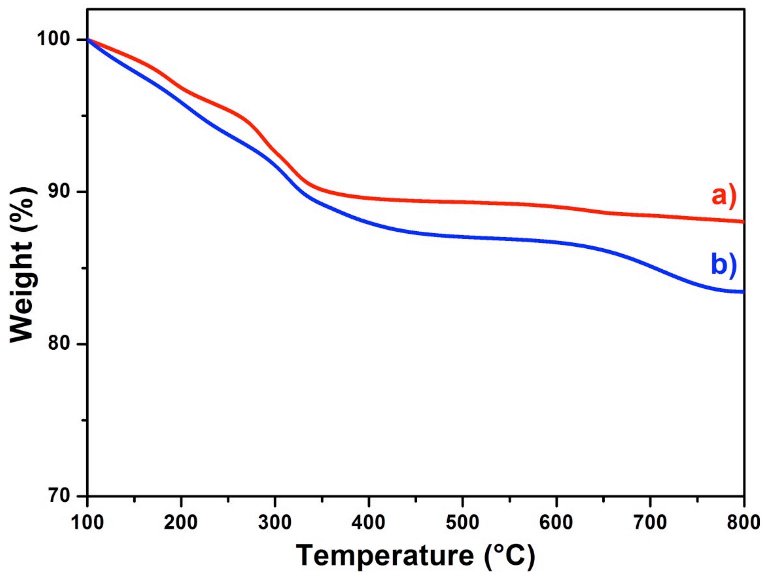

Figure S10. TGA curves of a) bare Fe_3O_4 MNPs without CB[n] modification; b) CB[6]-MNPs. TGA curves were obtained at nitrogen atmosphere with a heating rate of 10 K min^{-1}.

Table S1. Diameters and zeta potentials of MNPs measured by DLS

	Diameter (nm)		**Zeta Potential (mV)**	
Bared MNPs	454.4	461.1±9.1	-20.2	-25.4±4.5
	457.5		-27.6	
	471.5		-28.3	
CB[5]-MNPs	450.9	447.6±4.0	10.6	10.1±0.7
	448.6		9.27	
	443.2		10.5	
CB[6]-MNPs	512.6	513.2±20.6	17.8	19.2±1.6
	493.0		18.9	
	534.1		20.9	
CB[7]-MNPs	422.7	445.6±29.5	10.3	10.5±0.4
	478.9		10.2	
	435.2		10.9	
CB[8]-MNPs	424.3	448.4±38.0	14	14.8±0.8
	428.6		14.9	
	492.2		15.5	

$FeCl_3$ (0.325 g, 0.1 mmol) and CB[n]s (0.2 mmol) were first dissolved in ethylene glycol (20 mL), and NaAc (1.20 g, 14.6 mmol) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclaves were heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for several times.

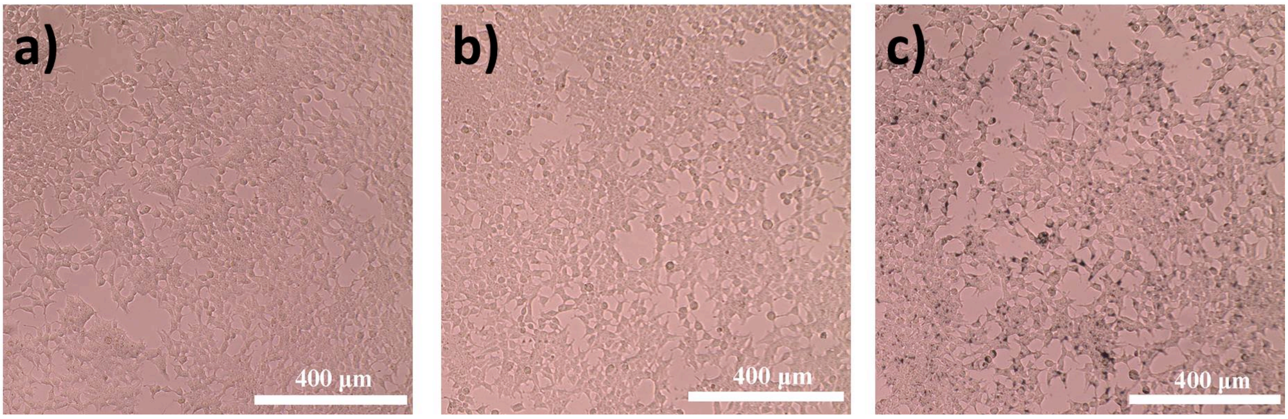

Figure S11. Cell micrographs of HEK 293T cells incubated with 25 μg mL^{-1} samples for 48 h: a) blank, b) CB[7], and c) CB[7]-MNPs.

3. Reference

S1. J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim. *J. Am. Chem. Soc.*, 2000, **122**, 540-541.